4.2 Elastic and inelastic neutron scattering

If the scattering system is assumed to be in thermal equilibrium at temperature T, the average over initial states in (4.1.16) is the same as the thermal average $\langle \cdots \rangle = \text{Tr}\{\rho_0 \cdots\}$, where ρ_0 is the density operator defined in eqn (3.1.1). The atom at the position $\widetilde{\mathbf{R}}_j = \mathbf{R}_j + \mathbf{u}_j$ vibrates around its equilibrium position, the lattice point \mathbf{R}_j , and we may write

$$\langle e^{-i\kappa \cdot (\widetilde{\mathbf{R}}_j - \widetilde{\mathbf{R}}_{j'})} \rangle = e^{-2W(\kappa)} e^{-i\kappa \cdot (\mathbf{R}_j - \mathbf{R}_{j'})},$$

where $W(\boldsymbol{\kappa})$ is the *Debye–Waller factor* $\approx \frac{1}{6}\kappa^2 \langle u^2 \rangle$, discussed in detail by, for example, Marshall and Lovesey (1971). We insert this term in (4.1.16), and thereby neglect contributions from inelastic phononscattering processes, the so-called magneto-vibrational part of the magnetic cross-section. The integral representation of the δ -function is

$$\delta(\hbar\omega + E_i - E_f) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i(\hbar\omega + E_i - E_f)t/\hbar} dt,$$

which allows us to write

$$\begin{split} \sum_{if} P_i < i \mid J_{j\alpha} \mid f > < f \mid J_{j'\beta} \mid i > \delta(\hbar\omega + E_i - E_f) \\ = \sum_{if} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{i\omega t} P_i < i \mid e^{i\mathcal{H}t/\hbar} J_{j\alpha} e^{-i\mathcal{H}t/\hbar} \mid f > < f \mid J_{j'\beta} \mid i > \\ = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{i\omega t} \sum_{i} P_i < i \mid J_{j\alpha}(t) \, J_{j'\beta}(0) \mid i > \\ = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{i\omega t} \langle J_{j\alpha}(t) \, J_{j'\beta}(0) \rangle, \end{split}$$

where $J_{j\alpha}(t)$ is the angular-momentum operator in the Heisenberg picture, as in (3.2.1),

$$J_{j\alpha}(t) = e^{i\mathcal{H}t/\hbar} J_{j\alpha} e^{-i\mathcal{H}t/\hbar}.$$

At thermal equilibrium, the differential cross-section can then be written

$$\frac{d^{2}\sigma}{dEd\Omega} = \frac{k'}{k} \left(\frac{\hbar\gamma e^{2}}{mc^{2}}\right)^{2} e^{-2W(\kappa)} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) \sum_{jj'} \{\frac{1}{2}gF(\kappa)\}_{j} \{\frac{1}{2}gF(-\kappa)\}_{j'} \times \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{i\omega t} e^{-i\kappa \cdot (\mathbf{R}_{j} - \mathbf{R}_{j'})} \langle J_{j\alpha}(t) \, J_{j'\beta}(0) \rangle. \quad (4.2.1)$$

If the magnetic atoms are all identical, the form factor may be taken outside the summation and the cross-section reduces to

$$\frac{d^2\sigma}{dEd\Omega} = N \frac{k'}{k} \left(\frac{\hbar\gamma e^2}{mc^2}\right)^2 e^{-2W(\kappa)} |\frac{1}{2}gF(\kappa)|^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) S^{\alpha\beta}(\kappa,\omega),$$
(4.2.2a)

where we have introduced the Van Hove scattering function (Van Hove 1954)

$$\mathcal{S}^{\alpha\beta}(\boldsymbol{\kappa},\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{i\omega t} \frac{1}{N} \sum_{jj'} e^{-i\boldsymbol{\kappa}\cdot(\mathbf{R}_j - \mathbf{R}_{j'})} \langle J_{j\alpha}(t) \, J_{j'\beta}(0) \rangle,$$
(4.2.2b)

which is $(2\pi\hbar)^{-1}$ times the Fourier transform, in space and time, of the pair-correlation function $\langle J_{j\alpha}(t) J_{j'\beta}(0) \rangle$. If $\langle J_{j\alpha} \rangle \langle J_{j'\beta} \rangle$ is added and subtracted, the scattering function may be written as the sum of a static and a dynamic contribution:

$$\mathcal{S}^{\alpha\beta}(\boldsymbol{\kappa},\omega) = \mathcal{S}^{\alpha\beta}(\boldsymbol{\kappa}) + \mathcal{S}^{\alpha\beta}_{d}(\boldsymbol{\kappa},\omega), \qquad (4.2.3a)$$

where the static or *elastic* component is

$$S^{\alpha\beta}(\boldsymbol{\kappa}) = \delta(\hbar\omega) \frac{1}{N} \sum_{jj'} \langle J_{j\alpha} \rangle \langle J_{j'\beta} \rangle e^{-i\boldsymbol{\kappa} \cdot (\mathbf{R}_j - \mathbf{R}_{j'})}$$
(4.2.3b)

and the inelastic contribution is

$$\mathcal{S}_{d}^{\alpha\beta}(\boldsymbol{\kappa},\omega) = \frac{1}{2\pi\hbar} S_{\alpha\beta}(\boldsymbol{\kappa},\omega) = \frac{1}{\pi} \frac{1}{1 - e^{-\beta\hbar\omega}} \chi_{\alpha\beta}^{\prime\prime}(\boldsymbol{\kappa},\omega).$$
(4.2.3c)

We have introduced the dynamic correlation function $S_{\alpha\beta}(\kappa,\omega)$, defined by eqn (3.2.13), with

$$\hat{\alpha} = N^{-\frac{1}{2}} \sum_{j} J_{j\alpha} e^{-i\kappa \cdot \mathbf{R}_{j}} \quad \text{and} \quad \hat{\beta} = N^{-\frac{1}{2}} \sum_{j'} J_{j'\beta} e^{i\kappa \cdot \mathbf{R}_{j'}},$$

and the corresponding susceptibility function $\chi_{\alpha\beta}(\boldsymbol{\kappa},\omega)$, utilizing the relation between the two functions given by the fluctuation-dissipation theorem (3.2.18).

An important consequence of (4.2.2-3) is that the *inelastic scat*tering of neutrons is proportional to the correlation function $S_{\alpha\beta}(\kappa,\omega)$, which is essentially the Fourier transform of the probability that, if the moment at site j has some specified vector value at time zero, then the moment at site j' has some other specified value at time t. An inelastic neutron-scattering experiment is thus extremely informative about the dynamics of the magnetic system. Poles in the correlation function, or in $\chi_{\alpha\beta}(\boldsymbol{\kappa},\omega)$, are reflected as peaks in the intensity of the scattered neutrons. According to (4.1.2) and (4.1.3), each neutron in such a scattering peak has imparted energy $\hbar\omega$ and momentum $\hbar\kappa$ to the sample, so the peak is interpreted, depending on whether $\hbar\omega$ is positive or negative, as being due to the creation or annihilation of quasi-particles or elementary excitations in the system, with energy $|\hbar\omega|$ and crystal momentum $\hbar \mathbf{q} = \hbar(\boldsymbol{\kappa} - \boldsymbol{\tau})$, where $\boldsymbol{\tau}$ is a reciprocal lattice vector. A part of the momentum $\hbar \tau$ may be transferred to the crystal as a whole. If the sample is a single crystal, with only one magnetic atom per unit cell, $S_{\alpha\beta}(\kappa,\omega) = S_{\alpha\beta}(\mathbf{q} = \kappa - \tau,\omega)$, where τ is normally chosen so that ${\bf q}$ lies within the primitive Brillouin zone. The form factor in the scattering amplitude is not however invariant with respect to the addition of a reciprocal lattice vector. This interpretation of the poles in $S_{\alpha\beta}(\mathbf{q},\omega)$ governs the choice of sign in the exponential arguments in both the temporal and the spatial Fourier transforms.

The relation (4.2.3*c*) between the scattering function and the generalized susceptibility implies that the neutron may be considered as a magnetic probe which effectively establishes a frequency- and wavevector-dependent magnetic field in the scattering sample, and detects its response to this field. This is a particularly fruitful way of looking at a neutron scattering experiment because, as shown in Chapter 3, the susceptibility may be calculated from linear response theory, and thus provides a natural bridge between theory and experiment. Using the symmetry relation (3.2.15), which may here be written $\chi^*_{\alpha\beta}(\mathbf{q}, z) =$ $\chi_{\alpha\beta}(-\mathbf{q}, -z^*)$, it is straightforward to show that $\chi''_{\alpha\beta}(\mathbf{q}, \omega) + \chi''_{\beta\alpha}(\mathbf{q}, \omega)$ is real and equal to $\mathrm{Im} \{\chi_{\alpha\beta}(\mathbf{q}, \omega) + \chi_{\beta\alpha}(\mathbf{q}, \omega)\}$. In addition, the form of the inelastic cross-section, and also the result (3.3.2) for the dissipation rate, impose another analytic condition on the function $\chi''_{\alpha\beta}(\mathbf{q}, \omega) + \chi''_{\beta\alpha}(\mathbf{q}, \omega)$. It must be either zero, or positive or negative with ω (such functions are called *herglotz functions*), because a negative value of the cross-section is clearly unphysical.

If the magnetic moments in a Bravais lattice are ordered in a static structure, described by the wave-vector \mathbf{Q} , we may write

$$\langle J_{j\alpha} \rangle = \frac{1}{2} \left(\langle J_{\alpha} \rangle e^{i \mathbf{Q} \cdot \mathbf{R}_j} + \langle J_{\alpha} \rangle^* e^{-i \mathbf{Q} \cdot \mathbf{R}_j} \right),$$
 (4.2.4)

allowing $\langle J_{\alpha} \rangle$ to be complex in order to account for the phase. The static contribution to the cross-section is then proportional to

$$\sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha} \hat{\kappa}_{\beta}) \, \mathcal{S}^{\alpha\beta}(\boldsymbol{\kappa}) = \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha} \hat{\kappa}_{\beta}) \operatorname{Re} \left\{ \langle J_{\alpha} \rangle \langle J_{\beta} \rangle^{*} \right\} \\ \times \, \delta(\hbar\omega) \frac{(2\pi)^{3}}{\upsilon} \sum_{\tau} \frac{1}{4} (1 + \delta_{Q0}) \left\{ \delta(\boldsymbol{\tau} + \mathbf{Q} - \boldsymbol{\kappa}) + \delta(\boldsymbol{\tau} - \mathbf{Q} - \boldsymbol{\kappa}) \right\},$$

$$(4.2.5)$$

where δ_{Q0} is equal to 1 in the ferromagnetic case $\mathbf{Q} = \mathbf{0}$, and zero otherwise, and v is the volume of a unit cell. The magnetic ordering of the system leads to δ -function singularities in momentum space, corresponding to magnetic Bragg scattering, whenever the scattering vector is equal to $\pm \mathbf{Q}$ plus a reciprocal lattice vector $\boldsymbol{\tau}$. The static and dynamic contributions from $S^{\alpha\beta}(\boldsymbol{\kappa})$ and $S_d^{\alpha\beta}(\boldsymbol{\kappa},\omega)$ to the total integrated scattering intensity may be comparable, but the dynamic contributions, including possibly a quasi-elastic diffusive term, are distributed more or less uniformly throughout reciprocal space. Consequently, the elastic component, determined by $S^{\alpha\beta}(\boldsymbol{\kappa})$, in which the scattering is condensed into points in reciprocal space, is overwhelmingly the most intense contribution to the cross-section $d\sigma/d\Omega$, obtained from the differential crosssection (4.2.2a) by an energy integration:

$$\frac{d\sigma}{d\Omega} \simeq N \left(\frac{\hbar\gamma e^2}{mc^2}\right)^2 e^{-2W(\kappa)} |\frac{1}{2}gF(\kappa)|^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) \operatorname{Re}\left\{\langle J_{\alpha}\rangle\langle J_{\beta}\rangle^*\right\} \\
\times \frac{(2\pi)^3}{\upsilon} \sum_{\tau} \frac{1}{4} (1 + \delta_{Q0}) \left\{\delta(\tau + \mathbf{Q} - \kappa) + \delta(\tau - \mathbf{Q} - \kappa)\right\}.$$
(4.2.6)

 $d\sigma/d\Omega$ is the cross-section measured in *neutron diffraction* experiments, in which all neutrons scattered in the direction of \mathbf{k}' are counted without energy discrimination, i.e. without the analyser crystal in Fig. 4.1. This kind of experiment is more straightforward to perform than one in which, for instance, only elastically scattered neutrons are counted. In the ordered phase, (4.2.6) is a good approximation, except close to a secondorder phase transition, where $\langle J_{\alpha} \rangle$ is small and where *critical fluctuations* may lead to strong inelastic or quasi-elastic scattering in the vicinity of the magnetic Bragg peaks.

Independently of whether the magnetic system is ordered or not, the total integrated scattering intensity in the Brillouin zone has a definite magnitude, determined by the size of the local moments and the following sum rule:

$$\frac{1}{N}\sum_{\mathbf{q}}\sum_{\alpha}\int_{-\infty}^{\infty}\mathcal{S}^{\alpha\alpha}(\mathbf{q},\omega)d(\hbar\omega)$$
$$=\frac{1}{N}\sum_{j}\sum_{\alpha}\langle J_{j\alpha}\rangle^{2}+\frac{1}{N}\sum_{\mathbf{q}}\sum_{\alpha}S_{\alpha\alpha}(\mathbf{q},t=0)$$
$$=\frac{1}{N}\sum_{j}\sum_{\alpha}\langle J_{j\alpha}J_{j\alpha}\rangle=J(J+1),$$
(4.2.7)

and taking into account the relatively slow variation of the other parameters specifying the cross-section. This implies, for instance, that $d\sigma/d\Omega$ is non-zero in the paramagnetic phase, when $\langle J_{\alpha} \rangle = 0$, but the distribution of the available scattered intensity over all solid angles makes it hard to separate from the background. In this case, much more useful information may be obtained from the differential cross-section measured in an inelastic neutron-scattering experiment.

For a crystal with a basis of p magnetic atoms per unit cell, the ordering of the moments corresponding to (4.2.4) is

$$\langle J_{j_s\alpha}\rangle = \frac{1}{2} \left(\langle J_{s\alpha}\rangle e^{i\mathbf{Q}\cdot\mathbf{R}_{j_s}} + \langle J_{s\alpha}\rangle^* e^{-i\mathbf{Q}\cdot\mathbf{R}_{j_s}} \right), \qquad (4.2.8a)$$

where

$$\mathbf{R}_{j_s} = \mathbf{R}_{j_0} + \mathbf{d}_s, \quad \text{with} \quad s = 1, 2, \cdots, p.$$
 (4.2.8b)

Here \mathbf{R}_{j_0} specifies the position of the unit cell, and \mathbf{d}_s is the vector determining the equilibrium position of the *s*th atom in the unit cell. The summation over the atoms in (4.2.2) may be factorized as follows:

$$\begin{split} \sum_{ij} e^{-i\kappa \cdot (\mathbf{R}_i - \mathbf{R}_j)} \\ &= \sum_{i_0 j_0} e^{-i\kappa \cdot (\mathbf{R}_{i_0} - \mathbf{R}_{j_0})} \sum_{s=1}^p e^{-i\kappa \cdot (\mathbf{R}_{i_s} - \mathbf{R}_{i_0})} \sum_{r=1}^p e^{i\kappa \cdot (\mathbf{R}_{j_r} - \mathbf{R}_{j_0})} \\ &= \sum_{i_0 j_0} e^{-i\kappa \cdot (\mathbf{R}_{i_0} - \mathbf{R}_{j_0})} |F_G(\boldsymbol{\kappa})|^2 \quad ; \quad F_G(\boldsymbol{\kappa}) = \sum_{s=1}^p e^{-i\kappa \cdot \mathbf{d}_s}, \end{split}$$

where $F_G(\kappa)$ is the geometric structure factor. The elastic cross-section then becomes

$$\frac{d\sigma}{d\Omega} = N_0 \left(\frac{\hbar\gamma e^2}{mc^2}\right)^2 e^{-2W(\kappa)} |\frac{1}{2}gF(\kappa)|^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) |\langle J_{\alpha}\rangle\langle J_{\beta}\rangle| \times \frac{(2\pi)^3}{\upsilon} \sum_{\tau} \frac{1}{4} (1+\delta_{Q0}) \operatorname{Re} \left\{ F_{\alpha}(\tau) F_{\beta}^*(\tau) \right\} \{ \delta(\tau + \mathbf{Q} - \kappa) + \delta(\tau - \mathbf{Q} - \kappa) \}$$

$$(4.2.9a)$$

where N_0 is the number of unit cells, and the *structure factor* is

$$F_{\alpha}(\boldsymbol{\tau}) = |\langle J_{\alpha} \rangle|^{-1} \sum_{s=1}^{r} \langle J_{s\alpha} \rangle e^{-i\boldsymbol{\tau} \cdot \mathbf{d}_{s}}.$$
 (4.2.9b)

As an example, we return to the Heisenberg ferromagnet discussed in Chapter 3. The magnitude of the ordered moments and their direction relative to the crystal lattice, defined to be the z-axis, may be determined by neutron diffraction, since

$$\frac{d\sigma}{d\Omega} = N \left(\frac{\hbar\gamma e^2}{mc^2}\right)^2 e^{-2W(\kappa)} |\frac{1}{2}gF(\kappa)|^2 (1-\hat{\kappa}_z^2) \langle S_z \rangle^2 \frac{(2\pi)^3}{\upsilon} \sum_{\tau} \delta(\tau-\kappa).$$
(4.2.10)

The Bragg-peak intensity is thus proportional to the square of the ordered moment and to $\sin^2 \theta$, where θ is the angle between the magnetization and the scattering vector. The elastic scattering is therefore strongest when $\kappa = \tau$ is perpendicular to the magnetization. On the other hand, the inelastic scattering is strongest when the scattering vector $\kappa = \mathbf{q} + \tau$ is along the magnetization, in which case, from (3.4.11),

$$\sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha} \hat{\kappa}_{\beta}) S^{\alpha\beta}(\boldsymbol{\kappa}, \omega) = \frac{1}{\pi} \frac{1}{1 - e^{-\beta\hbar\omega}} \left(\chi_{xx}^{\prime\prime}(\mathbf{q}, \omega) + \chi_{yy}^{\prime\prime}(\mathbf{q}, \omega) \right)$$
$$= \langle S_z \rangle \frac{1}{1 - e^{-\beta\hbar\omega}} \left\{ \delta(\hbar\omega - E_{\mathbf{q}}) - \delta(\hbar\omega + E_{\mathbf{q}}) \right\}$$
$$= \langle S_z \rangle \left\{ (n_{\mathbf{q}} + 1) \delta(\hbar\omega - E_{\mathbf{q}}) + n_{\mathbf{q}} \delta(\hbar\omega + E_{\mathbf{q}}) \right\}, \quad (4.2.11)$$

where $n_{\mathbf{q}} = (e^{\beta E_{\mathbf{q}}} - 1)^{-1}$ is the Bose population factor. The magnonscattering intensity is thus proportional to the ordered moment, and the *stimulated emission and absorption* of the boson excitations, i.e. the magnons, due to the neutron beam, are proportional respectively to $(n_{\mathbf{q}} + 1)$ and $n_{\mathbf{q}}$, which may be compared with the equivalent result for light scattering from a gas of atoms.



Fig. 4.2. A typical spectrum of inelastically-scattered neutrons in a constant- κ experiment, illustrating the determination of the dispersion relation and the polarization vector of the magnetic excitations. The peaks in the spectrum establish the energies of excitations which have a wave-vector \mathbf{q} , defined by the scattering vector through $\kappa = \mathbf{q} + \boldsymbol{\tau}$, and thus determine points on the dispersion relation for Pr, shown in Fig. 7.1. The cross-section is proportional to the factor $f(\alpha) = 1 - (\kappa_{\alpha}/\kappa)^2$. Since \mathbf{q} is along the ΓM (y)-axis, the absence of the peak of lower energy in the bottom figure shows unambiguously that it corresponds to a longitudinal mode.

The dependence of the intensity of inelastically scattered neutrons on the relative orientation of $\boldsymbol{\kappa}$ and the direction of the moment fluctuations is illustrated for the example of Pr in Fig. 4.2, which is discussed in more detail in Chapter 7. As in this figure, the scattering is normally measured as a function of $\hbar\omega$ at a fixed value of \mathbf{q} , a so-called *constant*- \mathbf{q} or *constant*- $\boldsymbol{\kappa}$ scan, but occasionally *constant*-energy scans may also be employed. In an actual experiment the directions and the lengths of **k** and **k'** are only defined with a limited degree of accuracy, and the δ -functions occurring in (4.2.10–11) are broadened into peaks with the shape of the *instrumental resolution function*, which to a good approximation is a Gaussian in the four-dimensional (κ, ω)-space. If the resolution function is known, it is possible to deconvolute the scattering peaks obtained in constant **q**-scans from the broadening due to instrumental effects, and thereby determine the lifetimes of the excitations.

In this chapter, we have concentrated on the magnetic scattering of neutrons, but they may also be scattered through the interaction, via nuclear forces, with the nuclei in the sample. This interaction leads to a cross-section of the same order of magnitude as in the magnetic case, and it results in analogous phenomena to those discussed above, with the positions of the atoms replacing the magnetic moments as the fluctuating variables. The elastic Bragg scattering reveals the positions of the atoms in the crystal, and the elementary excitations appearing in the correlation functions are phonons. The fluctuations in the nuclear cross-section, due to the different spin states of the nuclei, give rise to an *incoherent* scattering, determined by the self-correlation of the individual atoms, in contrast to the *coherent* scattering, which is governed by the atomic pair-correlation function, in analogy with the magnetic scattering discussed above. Incoherence can also be produced by different isotopes of a particular element in a crystal, just as the variation of the magnetic moments in disordered alloys leads to incoherent magnetic scattering.

The magnetic scattering may be difficult to separate experimentally from the nuclear component. One possibility is to utilize the different temperature dependences of the two contributions, since the nuclear scattering normally changes relatively slowly with temperature. If this is not adequate, it may be necessary to perform *polarized* neutron scattering, in which the spin states of the incoming and scattered neutrons are determined, making it possible to isolate the scattering of purely magnetic origin (Moon, Riste and Koehler 1969). For further details of neutron scattering by nuclei in solids we refer to the texts mentioned at the beginning of this chapter.